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EVALUATION OF UNIMOLECULAR RATE CONSTANTS FOR SOME
OUTER-SPHERE ELECTROCH. (U) PURDUE UNIV LAFAYETTE IN
DEPT OF CHEMISTRY M A TADAVYONI ET AL. JAN 85 TR-40
N00014-79-C-0670

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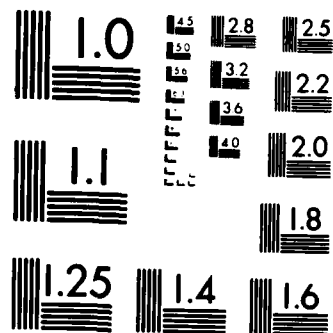
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TECHNICAL REPORT NO. 40

Evaluation of Unimolecular Rate Constants For
Some Outer-Sphere Electrochemical Reactions

by

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Prepared for Publication

in the

Journal of Electroanalytical Chemistry

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January 1985

FEB 28 1985

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER Technical Report No. 40		2. GOVT ACCESSION NO. AD-A150 758	
3. RECIPIENT'S CATALOG NUMBER		5. TYPE OF REPORT & PERIOD COVERED Technical Report No. 39	
4. TITLE (and Subtitle) Evaluation of Unimolecular Rate Constants for some Outer-Sphere Electrochemical Reactions		6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) M. A. Tadayoni and M. J. Weaver		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0670	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Purdue University West Lafayette, IN 47907		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, VA 22217		12. REPORT DATE January 1985	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public release; distribution unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES 7-1-85 (P-130)			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) precursor state, electrostatic work term correction, surface excess. a. 1270			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Unimolecular rate constants, k_{et} (sec^{-1}), and transfer coefficients, α_{et} , for the outer-sphere electroreduction of several Co(III) ammine and ethylenediamine complexes have been evaluated by electrostatically adsorbing the reactants at silver electrodes coated with chloride or bromide monolayers. Sufficiently strong diffuse-layer adsorption is thereby produced so to enable k_{et} and α_{et} to be determined by means of linear sweep voltammetry, employing sufficiently fast sweep rates ($10\text{--}100 \text{ V sec}^{-1}$) and dilute reactant concentrations ($\leq 50 \mu\text{M}$)			

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EVALUATION OF UNIMOLECULAR RATE CONSTANTS FOR
SOME OUTER-SPHERE ELECTROCHEMICAL REACTIONS

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ABSTRACT

Unimolecular rate constants, k_{et} (sec^{-1}), and transfer coefficients, α_{et} , for the outer-sphere electroreduction of several Co(III) ammine and ethylenediamine complexes have been evaluated by electrostatically adsorbing the reactants at silver electrodes coated with chloride or bromide monolayers. Sufficiently strong diffuse-layer adsorption is thereby produced so to enable k_{et} and α_{et} to be determined by means of linear sweep voltammetry, employing sufficiently fast sweep rates ($10\text{--}100 \text{ V sec}^{-1}$) and dilute reactant concentrations ($\leq 50 \text{ }\mu\text{M}$) so that the bulk solution reactant contributes negligibly to the observed faradaic transients. Comparison with corresponding rate constants and transfer coefficients for the solution reactants enables the influence of precursor-state stability upon the latter rate parameters to be assessed.

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A central problem in electrochemical kinetics, as for electron-transfer reactions in homogeneous solution, is to relate the observed rate parameters to the energetics of the various elementary steps that constitute the overall reaction. Even for one-electron redox couples where both the reactant and product are solution species, the reaction can generally be envisaged as taking place in two separate steps.¹ These involve the formation of a precursor state with the reactant situated at the interface in some spatial arrangement suitable for electron transfer, associated with a "precursor equilibrium constant" K_p (cm), followed by unimolecular activation of the reactant leading to electron transfer. The latter, "elementary electron-transfer", step is associated with a unimolecular rate constant, k_{et} (sec^{-1}). Providing that the second step is rate controlling and the first step is in quasi-equilibrium, the observed rate constant k_{ob} (cm sec^{-1}), i.e. that defined in terms of solution reactant concentration, can be expressed as¹

$$k_{ob} = K_p k_{et} \quad (1)$$

with

$$K_p = \Gamma_p / C_r \quad (2)$$

where Γ_p is the cross-sectional reactant concentration in the precursor state, and C_r is the corresponding bulk concentration after correction for diffusion polarization.

For inner-sphere reactions, i.e., those where the reactant is bound directly to the surface during the electron-transfer step, the precursor state is often sufficiently stable so that Γ_p is measurably large, enabling K_p to be determined directly. Values of k_{et} can therefore be obtained in such circumstances either by combining measurements of k_{ob} and K_p by

employing Eq. (1), or by evaluating k_{et} directly using electrochemical transient techniques.²⁻⁶

Although usually applied to inner-sphere processes, the preequilibrium model embodied in Eq. (1) is also applicable to outer-sphere reactions.³ Since Γ_p and hence K_p are commonly too small to be determined directly for outer-sphere reactions, resort is usually made to a double-layer model such as the Gouy-Chapman theory. Analogous considerations apply to bimolecular outer-sphere reactions in homogeneous solutions, where it is customary to estimate K_p by using the Debye-Huckel model.⁷ Nevertheless, Haim and coworkers have demonstrated that k_{et} values may be determined directly for homogeneous outer-sphere reactions involving multicharged ions of opposite sign, where the precursor ion pair is sufficiently stable to yield deviations from the usual second-order rate law.⁸

These results suggested to us that one possible means of determining unimolecular rate constants for outer-sphere electrochemical processes would be to examine multicharged cationic reactants at surfaces carrying sufficiently negative charge densities so that Γ_p for the cations can readily be evaluated. One difficulty with this procedure is that the occurrence of suitably large values of Γ_p usually require interfaces containing specifically adsorbed anions, for which the evaluation of Γ_p by thermodynamic means is severely complicated. Nevertheless, we have recently found that sufficiently negative diffuse-layer potentials are formed at silver-aqueous interfaces containing specifically adsorbed chloride or bromide anions so to generate extremely large surface concentrations of multicharged ammine complexes ($\Gamma_p > 1 \times 10^{-11} \text{ mol cm}^{-2}$) even at very small bulk concentrations ($C_r \sim 50 \text{ } \mu\text{M}$). Indeed, sufficiently large concentrations of the metal amines can be generated in the vicinity of the

outer Helmholtz plane (oHp) in this manner so to yield observable surface-enhanced Raman (SER) spectra for these complexes at silver electrodes.⁹

We report here the utilization of such halide-coated silver surfaces to evaluate unimolecular rate constants for the one-electron electroreduction of hexaamminecobalt(III), trisethylenediaminecobalt(III), and two pentaamminecobalt(III) complexes. These reactions have been of interest to us as "model outer-sphere" processes with which to examine the influence of the electrode material,¹⁰ and for comparison with closely related reactions involving ligand-bridged transition states.^{2,4,5,11}

Such Co(III) reductions have also played an important role in the development of structure-reactivity relationships for homogeneous redox processes.¹²

Sufficiently strong diffuse-layer adsorption is experienced so to enable k_{et} - potential data to be obtained conveniently using rapid linear sweep voltammetry, since negligible contributions to the measured faradaic current arise from the diffusing reactant under these conditions.^{3,4} These k_{et} values are compared with those for some structurally similar surface-attached reactants and with the corresponding k_{ob} values.

EXPERIMENTAL SECTION

The procedures used to synthesize and purify the Co(III) complexes (as perchlorate or chloride salts), are mostly as described in ref. 2; $\text{Co(en)}_3 \cdot \text{Cl}_3$ [en = ethylenediamine] was prepared as in ref. 13, and $\text{Ru(NH}_3)_6 \cdot (\text{ClO}_4)_3$ was recrystallized from the chloride salt (Matthey Bishop). The polycrystalline silver surface was fabricated in the form of a rotating disk electrode sheathed in Teflon, exposing a silver disk of area 0.125 cm^2 . This was employed for all stationary as well as rotating disk electrode measurements. The silver surface was electrochemically polished as described in refs. 10 and 14.

The rapid linear sweep voltammograms were obtained using a PAR 173/175/179 system as described in ref. 4; the data analysis is described in the Results section. This utilized sweep rates between 20 and 100 V sec⁻¹ along with dilute reactant concentrations ($C_r \sim 50 \mu\text{M}$) so to optimise the contribution to the measured faradaic current from the initially adsorbed, rather than the diffusing, reactant. The upper limit to the sweep rates employed (100 V sec⁻¹) was determined by the onset of distortion of the current-potential curves even in the presence of positive-feedback iR compensation. The rotating-disk voltammograms were obtained as in ref. 10. All electrode potentials are quoted with respect to the saturated calomel electrode (s.c.e.), and all kinetic measurements were performed at $24 \pm 0.5^\circ\text{C}$.

RESULTS AND DATA ANALYSIS

Figure 1 illustrates typical linear sweep voltammograms obtained for the reduction of Co(en)_3^{3+} at the silver-aqueous interface. Scan A is a cathodic-anodic sweep at 25 V sec⁻¹, from -200 mV to -800 mV vs sce, for 50 μM Co(en)_3^{3+} in 0.1 M NaClO_4 + 5 mM HClO_4 . [The acid is added to avoid precipitation of the Co(II) product on the electrode surface.] The virtually symmetrical and featureless current-potential curves obtained are essentially unaffected by the presence of the Co(III) complex even though Co(en)_3^{3+} is reduced in this potential region. This indicates, not unexpectedly, that reactant diffusion contributes negligibly to the measured current under these conditions.

However, substitution of the 0.1 M NaClO_4 , electrolyte by 0.1 M KCl yields the cathodic-anodic voltammogram shown in curve B. Besides the broad peak at ca 600 mV found in both negative- and positive-going potential scans, also seen in the absence of Co(en)_3^{3+} , a sharper peak is observed in

the former scan. The absence of the peak on the return scan is consistent with reduction of adsorbed Co(en)_3^{3+} since the rapid aquation of Co(II) following electron transfer¹⁵ renders the reaction irreversible on the cyclic voltammetric timescale. The assignment of this cathodic peak to reduction of initially adsorbed, rather than diffusing, reactant was confirmed by the essentially constant coulombic charge contained under the peak over the entire range of sweep rates employed.^{3,4} (This charge increased progressively for sweep rates below ca 10 V sec^{-1} , consistent with an emerging contribution from diffusing reactant.) Although detectable voltammetric peaks could be obtained using lower bulk reactant concentrations than $50 \text{ } \mu\text{M}$, this turned out to be a particularly efficacious choice.

Similar results were also obtained for the reduction of $\text{Co(NH}_3)_6^{3+}$, although somewhat (ca threefold) smaller adsorbed charges were deduced from the peak areas compared with those for Co(en)_3^{3+} . Some experiments utilized electrodes that were mildly roughened by means of an oxidation-reduction cycle¹⁴ in 0.1 M KCl following electrochemical polishing so to further enhance the contribution from adsorbed versus diffusing reactant. (Such an electrode pretreatment also yields measureable SER spectra.⁹) Essentially identical current-potential curves were obtained at electropolished and roughened electrodes once the increase in electrode area (i.e., the roughness factor, ca 1.5-2.5) was taken into account, as deduced from the increase in the background capacitance currents compared to those at the electropolished silver surface (cf ref. 14). Values of Γ_p were obtained from the faradaic cathodic charge density expressed in terms of the actual, rather than apparent (geometrical), electrode area; Γ_p equalled 3×10^{-11} and $9.5 \times 10^{-11} \text{ mol cm}^{-2}$ for $50 \text{ } \mu\text{M Co(NH}_3)_6^{3+}$ and Co(en)_3^{3+} , respectively. Further evidence for the presence of very high surface concentrations of

Co(en)_3^{3+} and $\text{Co(NH}_3)_6^{3+}$ is provided from the SER spectra obtained for these adsorbates under identical conditions.⁹

Values of k_{et} and their potential dependence, as expressed as the transfer coefficient $\alpha_{\text{et}} [= -(RT/F)(d\ln k_{\text{et}}/dE)]$, were extracted from the voltammograms as follows. Values of α_{et} were obtained from the dependence of the voltammetric peak potential, E^P , on the sweep rate, ν , using¹⁶ $\alpha_{\text{et}} = -(RT/F)(d\ln \nu/dE^P)$. This plot enables the values of k_{et} at any potential in the vicinity of E_p to be obtained from¹⁶

$$k_{\text{et}}^E = \alpha_{\text{et}} \nu_E F/RT \quad (3)$$

where ν_E is the sweep rate corresponding to a voltammetric peak potential to which k_{et}^E refers.

This analysis method therefore yields values of α_{et} and k_{et} at surface reactant concentrations, Γ_p , corresponding to the voltammetric peak; i.e., for about half the initial Γ_p value. Nevertheless, virtually identical α_{et} values are obtained for other coverages since the shape of the voltammograms is independent of the sweep rate. The k_{et} values at a given potential are also approximately independent of Γ_p (i.e., the kinetics are first order in the adsorbed reactant); this is demonstrated by estimating k_{et} values at various points on the voltammetric wave as described in ref. 4. Equivalently, essentially identical values of α_{et} to that acquired from the sweep rate dependence were obtained from the shape of a single voltammetric wave using¹⁶ $\alpha_{\text{et}} = 62.5/\Delta E$, where ΔE (mV) is the difference between the peak potential and that halfway up the rising part of the voltammetric wave. In contrast to the former, this latter method requires that the kinetics are first order in the adsorbed reactant.

Similar results were obtained using mixed perchlorate-chloride electrolytes with Cl^- concentrations down to ca 1 mM, although the voltammetric peaks were absent when smaller amounts of chloride were present. This is consistent with the chloride specific adsorption data at silver electrodes extracted under similar conditions from capacitance-potential measurements, which indicate that essentially a monolayer is obtained for chloride concentrations above ca 10 mM at electrode potentials positive of ca -200 mV.¹⁴ Similar values of Γ_p were obtained in electrolytes containing sufficient bromide to form a monolayer at silver.¹⁴

An alternative, although less quantitative, route to k_{et} utilizes rotating disk voltammetry. The voltammograms for the reduction of $\text{Co}(\text{NH}_3)_6^{3+}$, for example, in 0.1 M NaClO_4 + 5 mM HClO_4 at silver exhibit half-wave potentials, $E_{1/2}$, around -400 mV. Analysis of such voltammograms over a wide range of rotation speeds (100-2,000 r.p.m.) yield kinetics that are first order in the solution reactant concentration.¹⁰ Addition of increasing concentrations of chloride yields progressive positive shifts in the voltammetric wave. For $[\text{Cl}^-] \geq 0.1$ mM where a chloride monolayer is attained,¹⁴ the current-potential curves become independent of the chloride concentration, with $E_{1/2} \sim -100$ mV.¹⁷ Moreover, the faradaic currents on the rising part of the wave are also virtually independent of the reactant concentration; i.e., the reaction order approaches zero in the solution reactant concentration.

These zero-order kinetics suggest that the interfacial concentration, Γ_p , of $\text{Co}(\text{NH}_3)_6^{3+}$ (which determines the cathodic current density) approaches saturation. This is in harmony with SER spectra for $\text{Co}(\text{NH}_3)_6^{3+}$ obtained at the rotating silver electrode, which yields Raman intensities for adsorbed

$\text{Co}(\text{NH}_3)_6^{3+}$ that are independent of rotation speed and electrode potential over almost the entire rising portion of the voltammetric wave.¹⁸ This behavior is analogous to that for homogeneous bimolecular reactions between A and B, with A in large excess, where sufficiently stable ion pairs are formed so that the rate becomes independent of the concentration of A.⁸ In this case, the first-order rate constant as defined in terms of the concentration of B, [B], will equal k_{et} for the reaction since [B] then equals the required ion-pair concentration, [AB].⁸ However, for the analogous electrochemical case the concentration of heterogeneous "sites", [B'], is not known analytically, being determined in part by the properties of the incoming reactant A since the effective "heterogeneous ion-pair concentration" $[\text{AB}'] = \Gamma_p$, is influenced by lateral A-A interactions.

Approximate values of Γ_p can nevertheless be estimated from a simple packing model, yielding $\Gamma_p \sim 1-2 \times 10^{-10} \text{ mol cm}^{-2}$. This estimate of Γ_p together with the relevant current density, i_f , at a given potential where i_f is independent of C_r , yields estimates of k_{et} , from $k_{\text{et}} = i_f / F\Gamma_p$, that are within ca 2-3 fold of the corresponding values obtained directly from rapid linear sweep voltammetry.

Sufficient diffuse-layer adsorption can also be generated using conditions similar to those for $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ reduction so to enable values of k_{et} and α_{et} to be obtained by means of rapid linear sweep voltammetry for the one-electron reduction of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ (where OAc = acetate). A summary of the resulting rate parameters for all four Co(III) reduction reactions is given in Table I. The common electrode potential, -400 mV, was chosen so to avoid

extrapolation of the $\log k_{et} - E$ plots. Interestingly, similar values of Γ_p are generated for the dipositive cations $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ as for $\text{Co}(\text{NH}_3)_6^{3+}$. However, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ and $\text{c-Co}(\text{NH}_3)_4(\text{OH}_2)_2^{3+}$ reduction failed to yield detectable values of Γ_p ($\Gamma_p \leq 1 \times 10^{-11} \text{ mol cm}^{-2}$ for $C_r \leq 0.1 \text{ mM}$) by using rapid linear sweep voltammetry. This may be due in part to interference from capacitance peaks in the potential region, ca -200 to -300 mV, where reduction of these species is expected to occur. Similarly, no adsorption of $\text{Cr}(\text{bpy})_3^{3+}$ [bpy = 2,2'-bipyridine] could be detected even though reduction to Cr(II) occurs at -450 mV.

Nevertheless, detectable diffuse-layer adsorption was observed for $\text{Ru}(\text{NH}_3)_6^{3+}$ using this approach. Since reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ to $\text{Ru}(\text{NH}_3)_6^{2+}$ is rapid and reversible, symmetrical current-potential peaks were obtained in the cathodic and anodic directions. For $50 \text{ } \mu\text{M}$ $\text{Ru}(\text{NH}_3)_6^{3+}$ in 0.1 M KCl, $\Gamma_p \approx 3 \times 10^{-11} \text{ mol cm}^{-2}$. The formal potential of the adsorbed redox couple, E_a^f , was determined as -300 (± 5) mV from the peak potential. This can be compared with the corresponding bulk-phase formal potential, $E_b^f = -190 \text{ mV}$, extracted from cyclic voltammetry in 0.1 M KCl under conventional conditions. Identical results, expressed as capacitance-potential curves, were obtained from a.c. impedance measurements. (This is expected since the faradaic current associated with reversible adsorbed redox couples appears as a pure capacitance, rather than a resistive, component.) Thus addition of $50 \text{ } \mu\text{M}$ $\text{Ru}(\text{NH}_3)_6^{3+}$ to the halide electrolyte yielded a capacitance peak at -300 mV having the same shape and area (expressed as a charge density) as that obtained voltammetrically.¹⁹ The capacitance-potential profile on both sides of this peak was essentially unaffected by the addition of

$\text{Ru}(\text{NH}_3)_6^{3+}$, indicating that the extent of halide specific adsorption is not altered noticeably by the presence of the high $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ concentrations in the double layer. Confirmation that the voltammetric and capacitance peaks are associated with an adsorbed $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couple is obtained from the potential-induced SER frequencies for the metal-amine mode, which match quantitatively the redox equilibria data extracted from the electrochemical results.^{9,19}

DISCUSSION

Diffuse-layer adsorption of multicharged cationic reactants

At first sight it seems surprising that such strong adsorption could be induced from the influence of the diffuse layer alone. However, the following calculation demonstrates the plausibility of this effect. The ionic charge density, q'_x , corresponding to a monolayer of chloride or bromide anions is about $150 \mu\text{C cm}^{-2}$.¹⁴ This is offset somewhat by the positive electronic charge density residing on the metal surface, q^m . Estimates of q^m for the electrode potentials considered here, ca -200 to -450 mV vs sce, can be obtained by integrating the capacitance-potential data in ref. 14, yielding $q^m \sim 70 \mu\text{C cm}^{-2}$; this leads to an overall diffuse-layer charge density, $q_d = -(q'_x + q^m) \sim 80 \mu\text{C cm}^{-2}$.

Such large charges correspond to extremely negative diffuse-layer potentials, ϕ_d^{GC} , on the basis of the Gouy-Chapman model. Thus for a 0.1 M uni-univalent electrolyte (e.g., 0.1 M NaClO_4), $\phi_d^{\text{GC}} = -193 \text{ mV}$ at $q_d = 80 \mu\text{C cm}^{-2}$. (Accurate knowledge of q_d is unnecessary since the values of ϕ_d^{GC} are insensitive to q_d for $q_d \geq 40 \mu\text{C cm}^{-2}$.) The presence of very small bulk concentrations of multicharged cations, such as 50 μM of +3 or +2 ions considered here, are predicted to yield extremely large cation concentrations at the oHp from

electrostatic attraction. Estimation of the required interfacial concentrations, Γ_p (mol cm^{-2}), requires integration of the local three-dimensional (mol cm^{-3}) concentrations across the diffuse layer. Explicit expressions for the required $\phi^{\text{GC}} - x$ profile (where x is the distance from the o.H.p.) cannot be obtained in closed form, except at the o.H.p., since both the reactant and supporting electrolyte ions need to be considered. Nevertheless, approximate estimates of Γ_p were obtained by constructing the $\phi^{\text{GC}} - x$ profile from²⁰

$$\phi^{\text{GC}} = (4RT/F) \tanh^{-1} \exp(p - \kappa x) \quad (4)$$

with $p = \ln \tanh(F\phi_d^{\text{GC}}/4RT)$ (where ϕ_d^{GC} is calculated by including both reactant and supporting electrolyte ions) and κ is the reciprocal Debye length. (This relation assumes that the $\phi^{\text{GC}} - x$ profile is influenced only by the supporting electrolyte ions.)

The resulting reactant surface concentrations, determined from²⁰

$$\Gamma_p = \int_{x=0}^{\infty} C_r [\exp(-Z_r F \phi^{\text{GC}}/RT) - 1] dx \quad (5)$$

where Z_r is the reactant charge number, account well for the present experimental observations. Thus for $q_d = 80 \mu\text{C cm}^{-2}$ and $50 \mu\text{M}$ tripositive reactant, $\Gamma_p = 5 \times 10^{-10} \text{ mol cm}^{-2}$, and for $50 \mu\text{M}$ dipositive reactant, $\Gamma_p = 1.5 \times 10^{-10} \text{ mol cm}^{-2}$. Although the validity of such calculations are questionable at high diffuse-layer charges, they nonetheless demonstrate that such strong adsorption can be anticipated on simple electrostatic grounds. The smaller experimental values of Γ_p , 3 to $10 \times 10^{-11} \text{ mol cm}^{-2}$ (Table I), can be attributed to strong electrostatic repulsion within the cation layer at the oHp. (Note that a close-packed monolayer of ammine cations would constitute only about $4 \times 10^{-10} \text{ mol cm}^{-2}$.)

Also noteworthy is the similar values of Γ_p that are both predicted and observed for tripositive and dipositive reactants (Table I). This arises from a "buffering" action of the diffuse layer, whereby the presence of large interfacial concentrations of multicharged cations alters the diffuse-layer potentials so that the cathodic reactant charges are "leveled" to values approaching that required to balance the negative inner-layer charge.

Nevertheless, the influence of the chemical nature, as well as the charge, of the reacting cation is evidenced by the absence of detectable adsorption ($\Gamma_p \leq 1 \times 10^{-11}$ mol cm⁻²) for complexes containing aquo or bipyridine ligands. The especially large surface concentrations for ammine and ethylenediamine complexes may well be associated with ion-pairing interactions between the oHp cations and the specifically adsorbed anions. Indeed, ion-pair stability constants between ammine complexes and chloride ions are larger than those for similar aquo and polypyridine complexes.²¹

Interpretation of Unimolecular Rate Parameters.

It is of fundamental interest to compare such unimolecular outer-sphere rate parameters with the values for structurally similar surface-attached reactants as well as the rate parameters for the overall outer-sphere reactions. For this purpose it is desirable to define a "work-corrected" unimolecular rate constant, k_{et}^{corr} , which is related to the measured k_{et} values by

$$k_{et}^{corr} = k_{et} \exp(-\alpha_{et}^{corr} F\phi_r/RT) \quad (6)$$

where ϕ_r is the electrostatic potential at the reaction site, and α_{et}^{corr} is the work-corrected transfer coefficient related to α_{et} by

$$\alpha_{et}^{corr} = \alpha_{et} / [1 - (d\phi_r/dE)] \quad (7)$$

Equations (6) and (7) can be derived simply by noting that the effective potential difference experienced by the electron upon transfer from the metal surface to the reaction site is $(E - \phi_r)$ rather than E since the reactant is situated at a potential ϕ_r with respect to the bulk solution.

Since ϕ_r is required to be large and negative in order to undergo suitably large surface reactant concentrations, this "double-layer" correction will be significant. Nevertheless, ϕ_r for the present reactions at silver is readily obtained from the difference between the formal potentials for electrostatically adsorbed and bulk-phase $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $(E_a^f - E_b^f) = -110 \text{ mV}$. This estimate of ϕ_r is especially appropriate in view of the similar potentials at which the Co(III) reductions are monitored as well as their close structural correspondence to $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. Similar estimates, ca. -125 mV , are obtained by equating ϕ_r with ϕ_d^{GC} . The resulting values of k_{et}^{corr} , obtained

*A complication in equating $(E_a^f - E_b^f)$ simply with ϕ_r is that the diffuse-layer potential ϕ_d^{GC} is predicted to become more negative as the adsorbed $\text{Ru}(\text{NH}_3)_6^{3+}$ is reduced to $\text{Ru}(\text{NH}_3)_6^{2+}$. This difficulty is largely circumvented, however, since ϕ_r refers to $\text{Ru}(\text{NH}_3)_6^{3+}$ surface concentrations that are similar to those encountered for the Co(III) reductions.

from the experimental k_{et} values by using Eq (6) are given in Table I [The values of α_{et}^{corr} required in Eq (6) were obtained from the α_{et} values by using Eq (7) with $(d\phi_r/dE)$ being set equal to $(d\phi_d^{GC}/dE)$. The uncertainties in this correction are relatively small since typically $(d\phi_d^{GC}/dE) \lesssim 0.02$, so that $\alpha_{et}^{corr} \sim \alpha_{et}$.]

Of the systems in Table I, $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ reduction is particularly suited for comparisons with k_{et} values for surface-attached reactants since such data are available for a variety of thiocarboxylate-bridged pentaamminecobalt (III) reductions at several metal surfaces.^{4,22} Extrapolation of the rate data for the thiophenecarboxylate-bridged systems in ref 4 to the electrode potential employed in Table I, -400 mV, yields values of k_{et} that are roughly comparable to k_{et}^{corr} for the outer-sphere reduction of $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$, $5 \times 10^4 \text{ sec}^{-1}$. Thus for reactants featuring conjugated thiophene bridges at mercury electrodes, $k_{et} \sim 1 \text{ to } 3 \times 10^4 \text{ sec}^{-1}$. Since the smaller k_{et} values found with the latter bridges appear to be due to less efficient electron tunneling (i.e. to reaction nonadiabaticity),^{4,11,23} the similar k_{et}^{corr} value for $\text{Co}(\text{NH}_3)_5\text{OAc}^{2+}$ reduction might be taken as evidence for a nonadiabatic pathway for this reaction. It is equally likely, however, that these small or moderate differences between k_{et}^{corr} and k_{et} values for the outer- and inner-sphere reaction pathways, respectively, reflect other factors, such as the influence of a "surface thermodynamic" effect upon the latter quantities.⁴

As noted above, it is also instructive to compare the k_{et}^{corr} values for the outer-sphere reactions with the corresponding conventional rate constants, k_{ob} (cm sec^{-1}). It is usual to extract double-layer corrected rate constants, k_{corr} , from k_{ob} by using^{24,25}

$$\ln k_{corr} = \ln k_{ob} + (Z_r - \alpha_{corr}) F \phi_r / RT \quad (8)$$

$$\text{with } \alpha_{\text{corr}} = \frac{\alpha_{\text{ob}} - Z_r(d\phi_r/dE)}{1 - (d\phi_r/dE)} \quad (9)$$

where ϕ_r is the effective potential at the reaction site. Values of k_{corr} and α_{corr} at -400 mV at mercury electrodes, determined in this manner from rate parameters in perchlorate and/or hexafluorophosphate electrolytes^{10,25-28} (to minimise anion specific adsorption), assuming that $\phi_r = \phi_d^{\text{GC}}$, are also listed for the four reduction reactions in Table I. (See refs. 10, 25, and 27 for procedural details.) Similar values of k_{corr} and α_{corr} are also obtained for these reactions at silver electrodes.¹⁰

The relationship of $k_{\text{et}}^{\text{corr}}$ to k_{ob} is (cf Eq (1))¹:

$$k_{\text{corr}} = K_o k_{\text{et}}^{\text{corr}} \quad (10)$$

$$\text{where } K_o = K_p \exp(Z_r F \phi_r / RT) \quad (11)$$

The quantity K_o is simply the precursor stability constant corrected for electrostatic work terms. A virtue of Eq. (10) is that provided $k_{\text{et}}^{\text{corr}}$ is independent of the reaction environment (vide infra), comparison of these unimolecular rate constants with k_{corr} values evaluated at either the same or other metal-solution interfaces enable estimates of K_o to be obtained for the reactions in the latter environment.

The estimates of K_o obtained from the corresponding values of $k_{\text{et}}^{\text{corr}}$ and k_{corr} in this manner are also listed in Table I. Note that for the three Co(III) ammine reductions, $K_o \sim 10^{-7}$ cm, whereas $K_o = 2.5 \times 10^{-6}$ cm for Co(en)_3^{3+} reduction. For outer-sphere reactions we expect that²⁹

$$K_o \sim \chi + (\sim 5 \times 10^{-9} \text{ cm}) \quad (12)$$

where χ is the maximum distance beyond the plane of the closest approach (referred to the center of reactant) at which electron transfer can still occur via adiabatic pathways, (i.e., for which the electronic transmission coefficient, κ_{el} , remains close to unity). Some experimental evidence suggests that $\chi \lesssim 1-2 \times 10^{-8}$ cm for simple inner- and outer-sphere electrochemical reactions, including Co(III) ammine reductions.^{4,29,30} The larger K_o values for the Co(III) ammine reductions at mercury obtained here are similar to those for the outer-sphere reduction of Cr(III) amines extracted using a related analysis involving a comparison with k_{et} values for corresponding ligand-bridged reactions.²⁹

It is conceivable that these K_o values arise from especially large electrode-reactant tunneling distances for these reactions. However, it is more likely that they reflect the presence of interfacial Co(III) concentrations at the mercury-aqueous interface that are substantially (ca. 10-20 fold) higher than are expected on the basis of Eq. 11 with $\phi_r = \phi_d^{GC}$. In other words, the k_{corr} values in Table I are 10-20 fold too high as a result of the inadequacies of Eq. 11. Such enhanced surface concentrations can arise from penetration of the ammine complexes inside the oHp, or from the presence of reactant-interfacial solvent interactions that are more favorable than in bulk solution. The relatively close approach of such ammine reactants to the electrode surface is evidenced by the sensitivity of k_{ob} to alterations in the potential profile within the double layer.^{31,32}

The breakdown of Eq. (8) is almost certainly responsible for the very high (2.5×10^{-6} cm) estimate of K_o obtained for Co(en)_3^{3+} ; this is ca. 250 fold larger than expected from Eq. (12). This discrepancy is nicely compatible with the ca. 100-fold difference between the work-corrected standard rate constant for $\text{Co(en)}_3^{3+/2+}$ at the mercury-aqueous interface, $k_{corr}^s =$

$2.5 \times 10^{-2} \text{ cm sec}^{-1}$,²⁷ and the corresponding calculated quantity, $k_{\text{calc}}^s = 3 \times 10^{-4} \text{ cm sec}^{-1}$, obtained from electron-transfer theory.³³ The latter involves calculating the inner-shell barrier from structural parameters, and assumes that $K_0 = 5 \times 10^{-9} \text{ cm}$.³³ Such unexpectedly high interfacial concentrations of Co(en)_3^{3+} are also consistent with the distortions noted in the a.c. polarograms for this system, as well as the direct detection of adsorption at mercury electrodes from rapid cyclic voltammetry for closely related systems.^{34,35} Such complications appear to be absent in strongly solvating nonaqueous media, such as dimethylformamide and dimethylsulfoxide; indeed reasonable agreement between k_{corr}^s and k_{calc}^s is observed in these solvents.^{33,36}

It should be recognised that the validity of the present analysis does rely on the assumption that $k_{\text{et}}^{\text{corr}}$ depends only on electrode potential and not the surface environment. While this cannot be proven at present, the overall consistencies found in the present analysis do support its approximate validity.

Reasonably close agreement is seen between the corresponding values of α_{et} and α_{corr} in Table I, determined at the halide-coated silver and mercury interfaces, respectively. This suggests that α_{corr} is close to $\alpha_{\text{et}}^{\text{corr}}$, since as noted above $\alpha_{\text{et}} \sim \alpha_{\text{et}}^{\text{corr}}$. Thus although the *absolute* estimates of the double-layer correction at mercury from Eq. (8) are incorrect, the *potential derivatives* from Eq. (9) are apparently not greatly in error. This latter finding is nonetheless surprising since we expect that $\alpha_{\text{et}} \sim 0.5$ for simple electron-transfer processes.

Two related factors may account, at least in part, for the finding that $\alpha_{\text{et}} \sim 0.6-0.7$ for Co(III) ammine reductions. Although the formal potentials for these couples are unknown, they are probably comparable to the potentials at which α_{et} are determined, ca. -250 to -400 mV, on the basis of

$E_D^f = -460$ mV for $\text{Co(en)}_3^{3+/2+}$. Under such thermodynamically unfavorable conditions, values of α_{corr} around 0.6 are predicted from a harmonic oscillator model.* Nevertheless, the value of α_{corr} for $\text{Co(en)}_3^{3+/2+}$ is too large to rationalize on the basis, and may be attributable to partial kinetic control by the chemical equation step that follows the formation of Co(II) .

CONCLUSIONS

The present study illustrates how the normally onerous task of separating the observed rate constants for outer-sphere electrode reactions into the precursor stability and electron-transfer components can be achieved experimentally. Although the present approach is somewhat limited in scope, the evaluation of unimolecular rate parameters for such reactions is clearly worthy of further examination. In particular, it should be feasible to estimate Γ_p , and hence K_p and K_o , for outer-sphere processes featuring even small precursor-state concentrations by employing the methods of electrocapillary thermodynamics, allowing the determination of k_{et} when combined with k_{ob} measurements. Such approaches to the evaluation of K_p and k_{et} are being pursued further in this laboratory.

ACKNOWLEDGEMENTS

Computational assistance was provided by David Milner. This work is supported by the Air Force Office of Scientific Research and the Office of Naval Research. M.J.W. acknowledges a fellowship from the Alfred P. Sloan Foundation.

*This arises from the predicted asymmetry in the reactant and product free-energy curves associated with the larger metal-ligand force constants in the oxidized compared to reduced forms.³⁷ This ratio is ca. 1.9 for $\text{Co(NH}_3)_6^{3+/2+}$ from Raman spectral data,³⁸ similar to the system considered in ref. 37.

REFERENCES

1. J. T. Hupp, M. J. Weaver, *J. Electroanal. Chem.* 152 (1983), 1.
2. S. W. Barr, M. J. Weaver, *Inorg. Chem.* 23 (1984) 1657.
3. K. L. Guyer, M. J. Weaver, *Inorg. Chem.* 23 (1984) 1664.
4. T. T-T. Li, H. Y. Liu, M. J. Weaver, *J. Am. Chem. Soc.* 106 (1984) 1233.
5. M. J. Weaver, *Inorg. Chem.* 18 (1979) 402.
6. M. J. Weaver, F. C. Anson, *J. Electroanal. Chem.* 58 (1975) 95.
7. For example, G. M. Brown, N. Sutin, *J. Am. Chem. Soc.* 101 (1979) 883.
8. D. Gaswick, A. Haim, *J. Am. Chem. Soc.* 93 (1971) 7347; A. J. Miralles, R. E. Armstrong, A. Haim, *J. Am. Chem. Soc.* 99 (1977) 1416; A. J. Miralles, A. P. Szecsy, A. Haim, *Inorg. Chem.* 21 (1982) 697.
9. M. A. Tadayyoni, S. Farquharson, M. J. Weaver, *J. Chem. Phys.* 80 (1984) 1363.
10. S. W. Barr, K. L. Guyer, M. J. Weaver, *J. Electroanal. Chem.* 111 (1980) 41; K. L. Guyer, S. W. Barr, R. J. Cave, M. J. Weaver, in "Proc. Third Symp. Electrode Processes", S. Bruckenstein, J. D. E. McIntyre, B. Miller, E. Yeager (eds), *Electrochemical Society, Pennington, M. J., 1980*, p. 390.
11. S. W. Barr, K. L. Guyer, T. T-T. Li, H. Y. Liu, M. J. Weaver, *J. Electrochem. Soc.* 131 (1984) 1626.
12. For example, H. Taube, "Electron-Transfer Reactions of Complex Ions in Solution", Academic Press, N.Y., 1970, Chapter 3.
13. J. B. Work, *Inorg. Synth.* 2 (1953) 221.
14. J. T. Hupp, D. Larkin, M. J. Weaver, *Surface Science* 125 (1983) 429.
15. T. J. Swift, R. E. Connick, *J. Chem. Phys.* 37 (1962) 307.
16. A. J. Bard, L. R. Faulkner, "Electrochemical Reactions", Wiley, New York, 1980, p. 525.
17. D. Larkin, K. L. Guyer, J. T. Hupp, M. J. Weaver, *J. Electroanal. Chem.* 138 (1982) 401.
18. S. Farquharson, D. Milner, M. A. Tadayyoni, M. J. Weaver, *J. Electroanal. Chem.*, in press.
19. M. A. Tadayyoni, M. J. Weaver, in preparation.
20. P. Delahay, "Double Layer and Electrode Kinetics", Interscience, New York, 1965, Chapter 3.

21. For example, V. E. Mironov, Russ. Chem. Revs. 35 (1966) 455.
22. T. T-T. Li, M. J. Weaver, manuscript in preparation.
23. T. T-T. Li, K. L. Guyer, S. W. Barr, M. J. Weaver, J. Electroanal. Chem. 164 (1984), 27.
23. Ref. 20, Chapter 9.
24. M. J. Weaver, J. Electroanal. Chem. 93 (1978) 231.
25. M. J. Weaver, J. Phys. Chem. 84 (1980) 568.
26. S. Sahami, M. J. Weaver, J. Electroanal. Chem. 124 (1981) 35.
27. T. T-T. Li, M. J. Weaver, manuscript in preparation.
28. J. T. Hupp, M. J. Weaver, J. Phys. Chem. 88 (1984) 1463.
29. T. T-T. Li, M. J. Weaver, J. Am. Chem. Soc., in press.
30. M. J. Weaver, T. L. Satterberg, J. Phys. Chem. 81 (1977) 1772.
31. T. L. Satterberg, M. J. Weaver, J. Phys. Chem. 82 (1978) 1784.
32. J. T. Hupp, H. Y. Liu, J. K. Farmer, T. Gennett, M. J. Weaver, J. Electroanal. Chem. 168 (1984) 313; J. T. Hupp, M. J. Weaver, submitted for publication.
33. H. A. Laitinen, J. E. B. Randles, Trans. Far. Soc. 51 (1955) 54.
34. J. T. Hupp, H. T. Liu; P. A. Lay, W. H. F. Petri, A. M. Sargeson, M. J. Weaver, J. Electroanal. Chem. 163 (1984) 371.
35. J. K. Farmer, T. Gennett, M. J. Weaver, J. Electroanal. Chem., submitted.
36. J. T. Hupp, M. J. Weaver, J. Phys. Chem., in press.
37. K. H. Schmidt, A. Muller, Coord. Chem. Rev. 19 (1976) 41.

TABLE I Unimolecular Rate Parameters for Outer-Sphere Electroreduction of Co(III) Complexes at -400 mV vs. sce: Comparison with Conventional Rate Data.

Reactant	Γ_p^a mol cm ⁻²	α_{et}^b	k_{et}^c sec ⁻¹	$k_{et}^{corr^d}$ sec ⁻¹	α_{corr}^e	k_{corr}^f cm sec ⁻¹	K_o^g cm
Co(NH ₃) ₆ ³⁺	3x10 ⁻¹¹	0.68	3.5x10 ³	6x10 ⁴	0.65	4x10 ⁻³	7x10 ⁻⁸
Co(en) ₃ ³⁺	9.5x10 ⁻¹¹	0.9	50	2.5x10 ³	0.9	6x10 ⁻³	2.5x10 ⁻⁶
Co(NH ₃) ₅ F ²⁺	3x10 ⁻¹¹	0.65	5.5x10 ³	1.0x10 ⁵	0.6	6x10 ⁻³	6x10 ⁻⁸
Co(NH ₃) ₅ OAc ²⁺	3.5x10 ⁻¹¹	0.65	3x10 ³	5x10 ⁴	0.65	1x10 ⁻²	2x10 ⁻⁷

^aSurface reactant concentration at silver electrode, at -100 mV vs sce, corresponding to bulk reactant concentration of 50 μ M in 0.1 M KCl + 5 mM HClO₄.

^bTransfer coefficient for the electron-transfer step at silver electrode, determined from the linear sweep voltammetric peak potentials, E^p , as a function of the sweep rate, v , using $\alpha_{et} = -(RT/F)(d \ln v / d E^p)$ (see text and ref. 16).

^cUnimolecular rate constant for electron-transfer step at -100 mV vs sce at silver electrode, determined from linear sweep voltammetry using Eq. (3) (see text).

^dWork-corrected unimolecular rate constant at -100 mV vs sce; determined from k_{et} by using Eq. (9) with ϕ_r taken as -110 mV and $\alpha_{corr} \approx \alpha_{et}$ (see text).

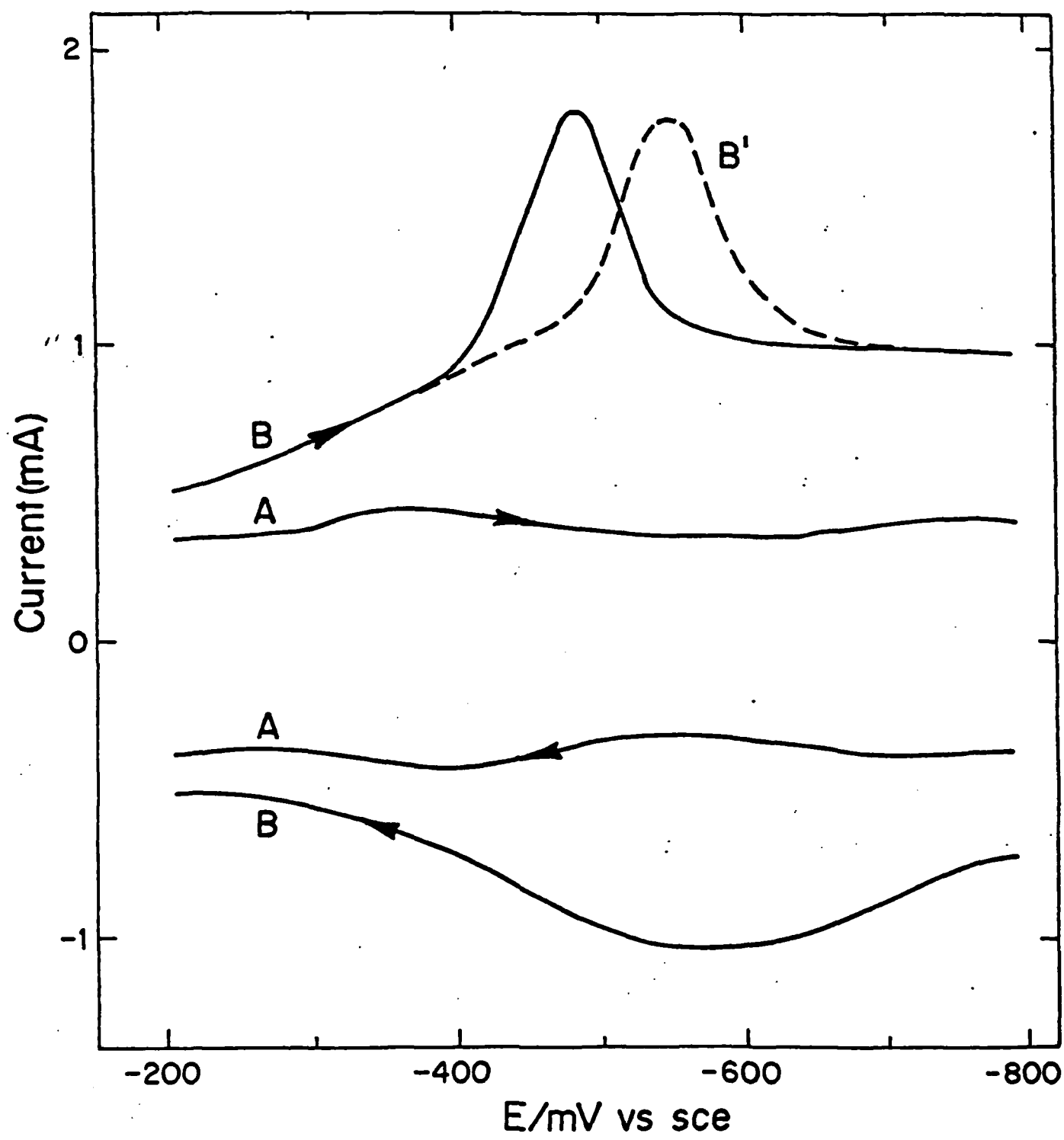
^eDouble layer-corrected transfer coefficient at mercury-aqueous interface. Determined from observed quantity, α_{ob} , in perchlorate and/or hexafluorophosphate electrolytes by using Eq. (9) with $\phi_r = \phi_d^{GC}$ (see text).

^fDouble layer-corrected rate constant at mercury-aqueous interface. Determined from experimental rate parameters in perchlorate and/or hexafluorophosphate electrolytes by using Eq. (8) with $\phi_r = \phi_d^{GC}$ and listed values of α_{corr} .

^g"Double layer-corrected" precursor stability constant at mercury-aqueous interface, determined from listed values of k_{corr} and k_{et}^{corr} by using Eq. (10).

Figure Caption

Fast cathodic-anodic cyclic voltammograms for reduction of Co(en)_3^{3+} adsorbed via chloride monolayer at silver electrodes. Curve A for $50 \mu\text{M}$ Co(en)_3^{3+} in $0.1 \text{ M NaClO}_4 + 5 \text{ mM HClO}_4$; curves B, B' for $50 \mu\text{M}$ Co(en)_3^{3+} in $0.1 \text{ M KCl} + 5 \text{ mM HClO}_4$. Sweep rate was 25 V. sec^{-1} for curves A and B, and 100 V. sec^{-1} for curve B'. Current scale for B' fourfold less sensitive than as shown for A and B. Apparent electrode area 0.13 cm^2 . Electrode roughened by single electrochemical oxidation-reduction cycle "as in ref. 14; effective roughness factor = 2.0.



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